Uranium migration through intact sandstone cores

D. Read[a], T.A. Lawless[b], R.J. Sims[b] and K.R. Butter[c]

[a]*WS Atkins Engineering Sciences, Epsom, Surrey, KT18 5BW, UK*
[b]*AEA Technology Winfrith, Dorset, DT2 8DH, UK*
[c]*Her Majesty's Inspectorate of Pollution, London, SW1P 3PY, UK*

ABSTRACT

Read, D., Lawless, T.A., Sims, R.J. and Butter, K.R., 1993. Uranium migration through intact sandstone cores. In: J.I. Kim and G. de Marsily (Editors), Chemistry and Migration of Actinides and Fission Products. J. Contam. Hydrol., 13: 277–289.

Uranium is often considered to be a mobile radioelement in the natural environment owing to its tendency to form stable complexes with a number of aqueous anions, particularly in oxidising milieu. A series of infiltration experiments were devised to investigate this migration behaviour under rigidly controlled laboratory conditions. Intact cores of Permo-Triassic Clashach Sandstone were pre-equilibrated with synthetic groundwater solutions and continuous flow-through of uranium monitored together with pH and concentrations of other ions.

Prior to performing each experiment a simulation was carried out using a one-dimensional coupled chemical transport code, encompassing a thermodynamic description of the electrical double layer. These calculations together with electron microscopy indicated the potential role played by iron oxyhydroxide grain coatings in retarding the uranium plume. Thus, a second series of experiments was initiated on pre-acidified cores from which all surface exposed iron had been removed, allowing an assessment of the retention capacity of non-ferric components.

Taken together, the data clearly illustrate the strong affinity of aqueous uranium species for natural surfaces even under strongly oxidising conditions. The success of the model in predicting a priori the dominant trends in uranium migration behaviour is encouraging and may aid in prioritising analytical requirements for investigations in more complex geochemical situations than those studied here.

1. INTRODUCTION

Procedures for assessing the long-term safety of proposed radioactive waste disposal facilities rely heavily on computer-based models which are used to predict the behaviour of contaminants within the repository, groundwater transport away from the repository and the effectiveness of host geologic media in ensuring adequate containment (Thompson, 1987). Although validation of such models in a predictive sense is rarely, if ever, feasible,

SW-A-004556

numerous attempts have been made to compare the results of simulation, retrospectively, with analytical data. The latter encompass static and dynamic laboratory experiments (Bidoglio et al., 1987). in situ field migration tests (Williams et al., 1991) and the study of natural analogues (Come and Chapman. 1991). Successful calibration is frequently cited as evidence of the model's accuracy even where key items of information are missing or the dominant processes operating are poorly understood.

In order to assess the confidence which can be ascribed to extant chemical transport models a series of simplistic column experiments have been devised to allow a priori prediction of trace-element migration through intact and very well-characterised sandstone cores. Column studies are regarded as an essential adjunct to observations made in the field. They possess the advantages of small scale and, as opposed to batch tests, representative solid/solution ratios. Additionally, when performed on intact samples there should be no alteration of microporosity and. hence. dispersivity and no creation of fresh surfaces which alter the inherent adsorption characteristics.

Uranium is often considered to be a mobile radioelement in the natural environment owing to its tendency to form stable complexes with aqueous anions. particularly in oxidising milieu. However, few attempts have been made to quantify this migration behaviour under controlled laboratory conditions and at the low concentrations typically found in groundwaters (Come and Chapman. 1991). Thus. the aims of the present work may be summarised as follows:

(1) to provide direct evidence of uranium mobilisation/retardation through rock samples relevant to waste disposal in the U.K.;

(2) to derive primary data for use in safety assessment calculations;

(3) to test the accuracy of results predicted in advance by an equilibrium chemical transport code and associated thermodynamic data.

The studies described are on-going and form part of a coordinated programme of research into the migration of naturally occurring radio-nuclides through geological media (Thompson. 1987). The results are also being adopted by participants in the Commission of European Communities (CEC) project CHEMVAL/MIRAGE (Read, 1991) for the purposes of model testing.

2. EXPERIMENTAL

2.1. Materials

The core material employed was Permo-Triassic Clashach Sandstone from the Elgin district of northeast Scotland. This rock is used extensively throughout the U.K. oil industry in the evaluation of production and enhanced oil recovery. The Clashach is a very well-sorted, supermature quartz

Fig. 1. Photomicrograph o

arenite comprising 1
overgrowths (Fig. 1). 1
the balance of the min:
and tourmaline. Fibr(
et al., 1992a). Iron ox:
samples. imparting an
is reflected in the whc

Column experimen
49-mm-diameter core:

TABLE 1

Elemental composition of

Element	(%)
Si	47
K	0.63
Al	<0.01
As	0.01
Ba	<0.02
Ca	<0.01
Cr	<0.01

re the results of simulation.
icompass static and dynamic
in situ field migration tests
ural analogues (Come and
uently cited as evidence of
formation are missing or the
stood.
ascribed to extant chemical
periments have been devised
tion through intact and very
tudies are regarded as an
he field. They possess the
batch tests. representative
med on intact samples there
hence, dispersivity and no
it adsorption characteristics.
radioelement in the natural
ble complexes with aqueous
er, few attempts have been
nder controlled laboratory
ally found in groundwaters
of the present work may be

lisation/retardation through
J.K.:
sessment calculations:
advance by an equilibrium
lynamic data.
rm part of a coordinated
naturally occurring radio-
1987). The results are also
n of European Communities
for the purposes of model

ic Clashach Sandstone from
s rock is used extensively
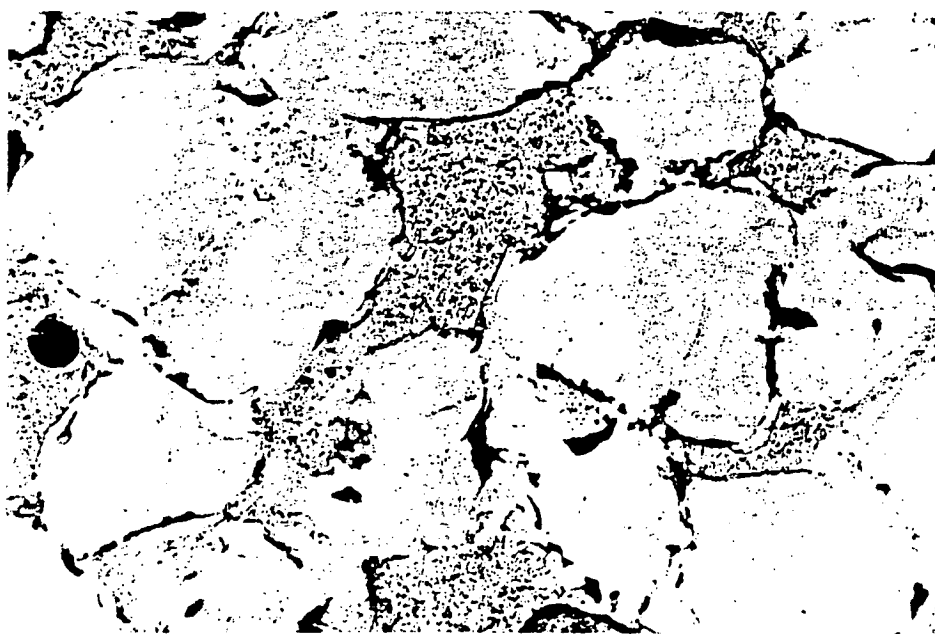luation of production and
l-sorted. supermature quartz

Fig. 1. Photomicrograph of Clashach Sandstone (×10).

arenite comprising rounded quartz grains (>95%) bonded by silica overgrowths (Fig. 1). Microcline and lithoclasts of quartzite or chert make up the balance of the mineralogy. together with infrequent grains of zircon, rutile and tourmaline. Fibrous illite has also been recorded but is scarce (Bennett et al.. 1992a). Iron oxide rims are observed to coat the quartz grains in some samples. imparting an orange-brown hue. The quartz-dominated mineralogy is reflected in the whole-rock analyses (Table 1).

Column experiments were performed on samples taken from 1-m-long, 49-mm-diameter cores. Each of these was sectioned to give two 30-cm cores

TABLE 1

Elemental composition of Clashach Sandstone core

Element	(%)	Element	(%)	Element	(%)
Si	47	Co	<0.01	P	<0.01
K	0.63	Cu	0.07	Sr	0.05
Al	<0.01	Fe	0.02	S	0.02
As	0.01	Mg	<0.01	Ti	<0.01
Ba	<0.02	Mn	<0.01	V	<0.01
Ca	<0.01	Mo	<0.01	Zn	<0.01
Cr	<0.01	Ni	<0.02	Zr	<0.01

TABLE 2

Properties of the sandstone cores

Column	1	2	3
Length (cm)	30	30	30
Diameter (cm)	4.9	4.9	4.9
Flood duration (days)	25	20	25
Brine permeability (mD)	330	400	480
Pore volume (cm^3)	82.4	103.8	96
Interstitial velocity (cm day^{-1})	300	300	300
Surface area ($m^2 g^{-1}$)	1.2	0.9	0.8
Cation exchange capacity (meq/100 g)	0.06	0.1	0.09
Anion exchange capacity (meq/100 g)	<0.01	<0.01	<0.01
Inlet U (10^{-8} mol dm^{-3})	1.0	1.0	1.0
Outlet U (10^{-8} mol dm^{-3})	<0.2	<0.02	<0.2
Inlet Cd (10^{-4} mol dm^{-3})	–	–	0.9
Outlet Cd (10^{-4} mol dm^{-3})	–	–	0.9

for uranium floods. three 7.5-cm cores for porosity determinations and a number of slices for wet analysis and thin-section studies. The hydrologic and ion-exchange characteristics of the intact sample are given in Table 2.

A synthetic sodium chloride solution similar to that encountered at outcrop was used in the experiments. doped with uranyl dinitrate and. for dispersion studies. ^{36}Cl. Inlet and outlet solutions were ultrafiltered using Amicon Diaflo" membranes (~ 2 nm) to monitor the removal of any uranium-bearing particulates.

2.2. Procedure

The experimental set-up is described in detail elsewhere (Bennett et al.. 1992a). Briefly, the first core was vacuum filled with NaCl and flushed continuously until the inlet and outlet concentrations had stabilised. ^{36}Cl tracer was then injected to generate a dispersion profile for the core. The uranium flood was performed at a rate of 35 cm^3 h^{-1} and an equivalent U concentration of 10^{-8} mol dm^{-3}. Analysis of the inlet and effluent solutions was carried out, using isotope dilution mass spectrometry (IDMS) for uranium and inductively coupled plasma optical spectrometry (ICPOS) for the other elements determined (As, Ba, Ca. Co, Cu. Fe, K, Mg, Mn, Mo. Na, P, Si, Sr, Ti, V, Zn. Zr). After 25 days the flood was stopped and twenty 3-mm slices taken from the inlet end of the core. Uranium and the other elements were analysed following extraction with nitric and hydrochloric acids. Experimental parameters are summarised in Table 2.

The second flood was performed on an acidified core. The column was first

filled with 0.3 mol dm^{-3} NaCl, for determination of initial permeability and then flooded with 0.1 M HCl in NaCl until the pH, as determined on-line, approached pH 1. Effluent fractions were monitored during acidification for released cations. The acid injection was stopped and flooding with NaCl continued until the effluent pH recovered to the inlet value. The second uranium flood was carried out at 43 cm^3 h^{-1} and terminated after 20 days.

Finally, a third flood was performed on a section of an additional core to assess the effect of competing cations on uranium transport. Cadmium chloride (10^{-4} mol dm^{-3}) was chosen for contemporaneous injection with 10^{-8} mol dm^{-3} uranium nitrate. Again, porosity, permeability, surface area and CEC measurements were performed on the core.

3. THEORETICAL CONSIDERATIONS

A central objective of this study is an appraisal of the predictive capability of extant equilibrium models when applied to the transport of actinides at realistic environmental concentrations. A level of 10^{-8} mol dm^{-3} U (2 ppb) is typical for terrestrial groundwaters (Hooker, 1991) but much lower than that commonly employed in batch sorption experiments (e.g., Berry et al., 1991). Under strongly oxidising conditions, as observed in the Clashach columns, it is also a level well below the limiting concentration imposed by any potential solubility controlling phase. Predictions of solubility using the PHREEQE code (Parkhurst et al., 1980) and thermodynamic data from published sources (Wolery, 1988; Read, 1991; Grenthe et al., 1992) give estimates around 10^{-4} mol dm^{-3} at equilibrium with schoepite ($UO_2(OH)_2 \cdot H_2O$), comparable to those reported by Sandino (1991). Other common uranium solids, including uraninite (UO_2) and rutherfordine (UO_2CO_3) are calculated to be strongly undersaturated. These results together with the absence of uranium-bearing particulates (Bennett et al., 1992a) indicate transport in "true" aqueous solution subject to retardation by surface adsorption. This is the basis for the numerical simulations described below.

The speciation of uranium in near-neutral waters has been studied extensively in recent years and the dominant controls on aqueous complexation established (e.g., Sandino, 1991). Using the CHEMVAL thermodynamic database (Chandratillake et al., 1992), uranyl(VI) hydroxy complexes are predicted to dominate around pH 6 with monomeric species favoured at the low solution concentration considered in this work. Under more strongly acid conditions the uncomplexed uranyl ion becomes increasingly important (Table 3). Carbonate complexation becomes significant at pH $\geqslant 7$.

Chemical transport modelling was carried out using the CHEMTARD code (Bennett et al., 1992b) and a triple-layer representation of the sorbing oxide

TABLE 3

Predicted distribution of uranium species at 10^{-8} mol dm^{-3}

Species	Concentration (%)	Reaction	$\log \beta$
UO_2^{2+}	54	$U^{4+} + 2H_2O - 4H^+ - 2e$	-9.2
UO_2OH^+	32	$U^{4+} + 3H_2O - 5H^+ - 2e$	-14.5
UO_2Cl^+	13	$U^{4+} + 2H_2O + Cl^- - 4H^+ - 2e$	-8.7

surface (Davis et al., 1978). The latter was assumed to approximate to goethite for the case of the unacidified core and silica following acidification, respectively.

The surface complexation model contained in CHEMTARD has been described in earlier work (Hooker, 1991). Briefly, the model considers a neutral surface (SOH) which can dissociate to give a negatively charged site:

$$SOH \rightleftharpoons SO^- + H_s^+ \tag{1}$$

where the subscript s denotes an ion located at the surface plane or, conversely, react with a proton at the surface to form a positively charged site:
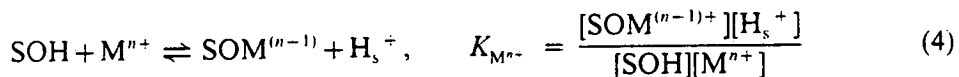
$$SOH + H_s^+ \rightleftharpoons SOH_2^+ \tag{2}$$

The activity of H^+ in the surface plane is related to the activity in the bulk solution by:

$$(H_s^-) = (H^+)\exp(-e\psi_i/kT) \tag{3}$$

where ψ_i is the change of potential when a species moves from the bulk solution to the solid phase; e is the electronic charge; k is the Boltzmann constant; and T the temperature in kelvins.

Mass action terms are written for binding of cations or anions with the surface but in this case, the bound ions are assumed to be located in the ß-plane (Davis et al., 1978). For cations:

$$SOH + M^{n+} \rightleftharpoons SOM^{(n-1)} + H_s^+, \qquad K_{M^{n-}} = \frac{[SOM^{(n-1)+}][H_s^+]}{[SOH][M^{n+}]} \tag{4}$$

In a manner analogous to deprotonation reactions, activity at the ß-plane is related to that in the bulk solution by:

$$[M_\beta^+] = [M^+]\exp(-e\psi_\beta/kT) \tag{5}$$

where ψ_β is the change in potential in moving from the bulk solution to the ß-plane. The model is discussed in detail elsewhere (Davis et al., 1978).

A database comprising the constants necessary to implement the Triple-Layer Model (TLM) has been compiled as part of the U.K. DOE radiological

TABLE 4

Intrinsic equilibrium constants (Djafer et al., 1989) for sorption onto α-FeOOH and SiO_2*

Reaction	$\log K$
$FeOH + Na^+ \rightleftharpoons FeO-Na + H^+$	-8.4
$SiOH + Na^+ \rightleftharpoons SiO-Na + H^+$	-7.1
$SOH + H^+ + Cl^- \rightleftharpoons SOH_2-Cl$	7.0
$SOH + Cd^{2+} \rightleftharpoons SO-Cd^+ + H^+$	-3.0
$SOH + UO_2^{2+} \rightleftharpoons SO-UO_2^+ + H^+$	-1.8
$SOH + UO_2OH^+ \rightleftharpoons SO-UO_2OH + H^+$	-2.7

*Where the range of quoted data does not allow a distinction to be made between sorbing surfaces. a composite (SOH) value was used. Surface deprotonation constants employed in the modelling study were 4.5 (pK_1) and 12.0 (pK_2) for the unacidified core. 1.5 and 8.5 for the acid washed core. respectively. Interlayer capacitances were 100 and 20 $\mu F\,cm^{-2}$. Auxiliary thermodynamic data taken from Chandratillake et al. (1992).

assessment programme (Economides et al., 1990). More than 150 specific adsorption constants are included with emphasis on the major groundwater components, uranium and thorium. Sorption equilibria considered in this work are summarised in Table 4.

4. RESULTS AND INTERPRETATION

4.1. Properties of the sandstone column

The Clashach is an equigranular, homogeneous sandstone and this is reflected in the constancy of porosity measurements and the dispersion profiles for ^{36}Cl tracer (Fig. 2; Péclet number $\simeq 100$). Porosity measurements are $\sim 20\%$ and permeability for the unacidified cores, 0.3 D. Porosity increased slightly to 22% upon acidification but this was not matched by changes in surface area or dispersivity (Fig. 2).

Cation- and anion-exchange capacities were found to be < 0.1 meq/100 g (Table 2) in agreement with the low clay content. Nevertheless, more than 50 pore volumes of 0.1 mol dm^{-3} HCl were required to achieve pH 1 in the effluent. demonstrating the strong buffering capacity of even clean, almost monomineralic sandstone. For this reason, uranium migration experiments were carried out at the "natural" pore-water pH of the Clashach Sandstone, pH ≈ 5.6.

4.2. Uranium migration

4.2.1. First column. Simulation of uranium transport was carried out a priori using the CHEMTARD code (Bennett et al., 1992b) and adsorption data for the
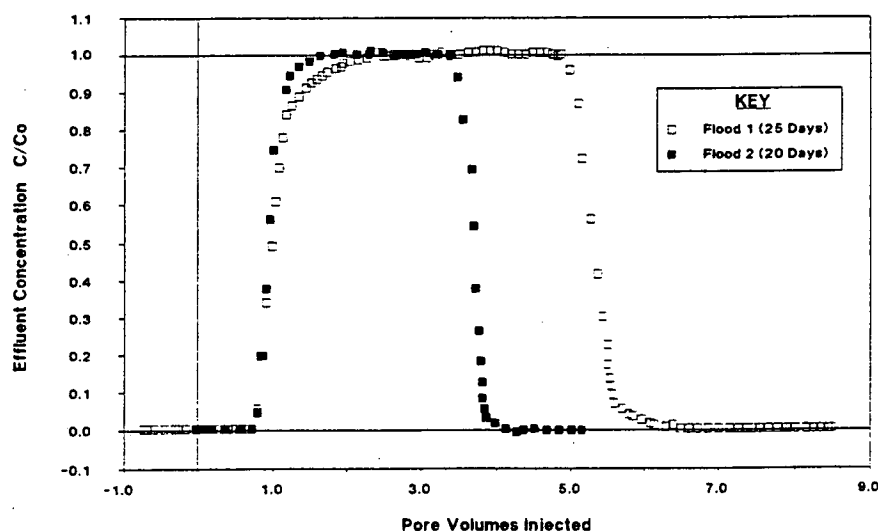
Fig. 2. Dispersion profiles (^{36}Cl) for Clashach Sandstone.

principal uranium aqueous species listed in Table 4. For the first flood, adsorption was assumed to be dominated by the presence of iron oxide coatings surrounding the quartz grains with a surface area of 1 m^2 g^{-1}. equivalent to $8 \cdot 10^3$ m^2 dm^{-3} in the pore fluid. Measurements of cation-exchange capacity were used as a guide to the concentration of surface sites available for uranium uptake, estimated to be in the region of 0.01–0.1 eq dm^{-3}.

Previous column studies on neptunium migration indicated chromato-graphic breakthrough of contaminant species owing to the non-attainment of equilibrium on the timescale of the experiments (Bidoglio et al., 1987). Two sets of simulations were performed, therefore, in order to take account of slow kinetic effects, representing complete local equilibrium and effectively no equilibrium between transported species, respectively. In the case of uranium, the alternative approaches produce similar results, although attenuation is greater for the local equilibrium simulation. For calculations at pH $\geqslant$ 5.5, no breakthrough is predicted after 25 days, with most of the uranium introduced to the column retained close to the source (Fig. 3). The model results are obviously affected by estimates of both surface area and site density. Additionally, the extent of uranium transport is very sensitive to the charge on the amphoteric surface. The latter is governed, in turn, by the shape of the deprotonation curve and the ambient pH. Intrinsic deprotonation constants obtained by various workers are listed in Table 5.

The above findings are borne out by the experimental data, though the model tends to overestimate the extent of uranium transport. As predicted, no
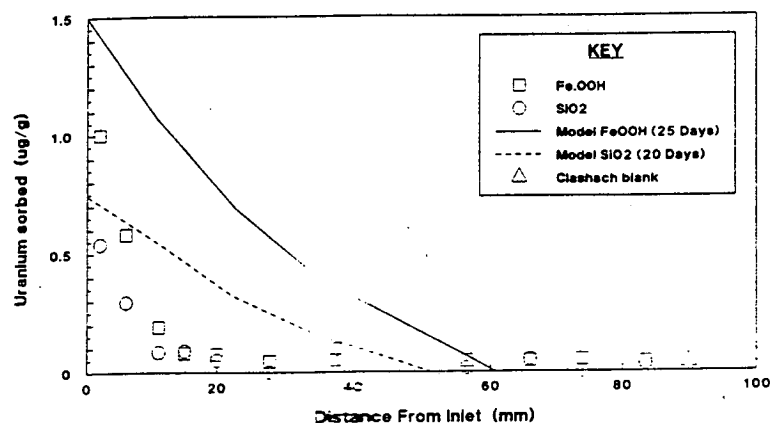
Fig. 3. Uranium sorbed on sectioned cores, before and after acidification.

discernible uranium reached the outlet. Analysis of sections taken at intervals along the core show that the majority of the uranium was adsorbed within a few millimetres of the inlet (Fig. 3) and ~65% of the injected uranium was contained in the first five 3-mm slices (Bennett et al., 1992a). A more precise mass balance is difficult given the low concentrations observed and the wastage involved in preparing sections for analysis. Of the other elements determined only Ba, Mg, Si and Zn are above the limit of detection in the effluent solution where they occur at concentrations comparable to those at the inlet.

4.2.2. Second column. The assumption that surficial iron was responsible for retardation appears reasonable on the basis of the known affinity of sesquioxides for uranium in natural waters (Hooker, 1991). However, iron oxide is not ubiquitous in the Clashach and it was decided to verify this assumption, therefore, by repeating the experiment on an acidified core from which surface iron had been removed.

Monitoring the effluent after acidification showed a rapid leaching of several trace elements (Bennett et al., 1992a) followed by a decrease to

TABLE 5

Deprotonation constants for oxide surfaces (Djafer et al., 1989)

Surface	$\log K_{1(INT)}$			$\log K_{2(INT)}$		
FeOOH	−4.2	–	−5.7	−9.5	–	−12.0
SiO₂		~1.0		−6.4	–	−7.2
Al₂O₃	−5.2	–	−5.7	−11.5	–	−11.8
TiO₂	−2.6	–	−3.2	−8.7	–	−9.1

background inlet values after ~ 20 pore volumes. Interestingly, the iron profile had a longer tail than the other trace elements studied suggesting the presence of minor crystalline phases, resistant to acid leaching. This has been confirmed by dissolution of the sectioned core.

Predictions of uranium transport were carried out as before, taking silica to be the sorbing phase in the acidified sandstone. Again no breakthrough was predicted on a 20-day timescale owing to strong uptake of U(VI) cations on the negatively charged surface (Table 5). Indeed, the lower zero point of charge (ZPC) for silica leads to model results in which migration is less than in the first flood.

Analysis of uranium extracted from sections of the core corroborates the simulations (Fig. 3). Though the mass balance is poorer than for the unacidified core, it is clear that little uranium extends beyond 20 mm of the source. Measurements of iron show a rapid drop from a concentration much lower than in the first flood to below the detection limit, implying that almost all accessible iron had been removed by acidification (Bennett et al., 1992a).

In actuality, both silica and iron oxyhydroxides are likely to effect uranium retention within the Clashach Sandstone. Further experimental work is required to determine their relative contribution and the composite. intrinsic adsorption properties of the prepared cores.

4.2.3. Third column. The conditions under which trace concentrations of uranium could move through the sandstone are now being investigated. As noted in Section 4.1 (p.283), the Clashach is very well buffered such that experiments carried out at artificially high or low pH would not produce results which are representative of the undisturbed system. Given this, the dominant factors likely to promote uranium mobilisation are:

(1) significant concentrations of ions which compete for adsorption sites;
(2) the presence of aqueous complexants which inhibit surface abstraction.

The latter was studied by Berry et al. (1991). for example, who noted reduced sorption of uranium onto Caithness sandstones (Scotland, U.K.) following treatment with gluconate or cellulose degradation products. Similar investigations on the Clashach Sandstone form the subject of on-going research. Preliminary results of research into the effect of competing ions are described briefly below.

Cadmium was chosen as the competing cation in view of the fact that its adsorption onto geological materials has been studied extensively (Economides et al., 1990) and data for interaction with oxide surfaces are available (Djafer et al., 1989). These studies show that relatively little uptake occurs at pH $\leqslant 5$ but abstraction increases sharply under neutral to alkali conditions. The predicted effect of cadmium on uranium sorption at pH 6 is
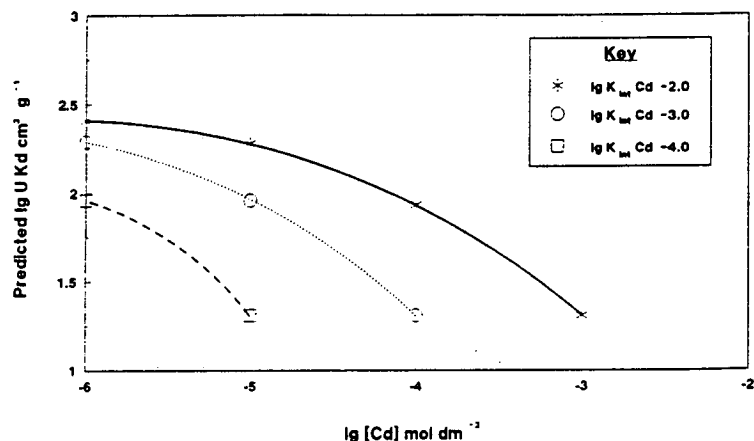
Fig. 4. Predicted variation in uranium K_d as a function of competing cadmium concentration.

shown in Fig. 4. for various cadmium concentrations and intrinsic adsorption constants quoted in the literature (Djafer et al., 1989).

The model results indicate that a cadmium level of 10^{-5} mol dm^{-3} would substantially reduce uranium uptake onto silica. Therefore, a further series of simulations was performed to investigate the effect of this competition on dynamic transport through the sandstone columns. Fig. 5 plots concentration vs. distance profiles in the presence and absence of cadmium, from which it can be seen that the uranium plume is predicted to move more than twice as far in the former case owing to competition. Cadmium, itself, is comparatively mobile, appearing in the effluent after 1 day (Bennett et al., 1992a).

Experimental results are inconclusive for the U–Cd–sandstone system owing to resolution problems with low uranium levels in the small core. As
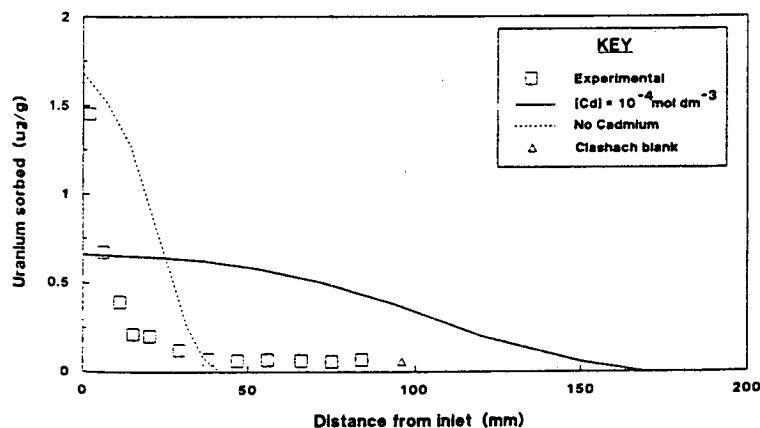

Fig. 5. Uranium sorbed on sectioned core following simultaneous injection of cadmium.

with the two columns described previously, no uranium breakthrough occurred and most of the uranium was retained close to the inlet. It is not apparent at this stage, whether or not cadmium promotes migration of the uranium plume downstream.

5. CONCLUSIONS

Immobilisation of uranium under reducing conditions is well established. Although by no means complete, this study also demonstrates the strong affinity of natural surfaces for aqueous uranium species under strongly oxidising conditions. No breakthrough occurred with the columns studied even where the already pure quartz sandstone was acid washed. By implication, migration of uranium at comparable levels through more heterogeneous clastic material is likely to be severely impeded.

The ability of a chemical transport model to predict a priori trace uranium transport through the Clashach Sandstone was critically dependent upon quantitative data being available to characterise column hydrology, sorption area, site density and the variation of surface charge with pH. For the simple system investigated here, the model proved relatively effective. Although it is unrealistic to expect the same level of characterisation for field systems, the application of thermodynamic models and data is felt to be far preferable to the use of purely empirical "retardation factors". The former may be used to predict trends in migration behaviour, if not the magnitude, thereby allowing priorities to be defined for analytical work. In the present context, these include studying the migration of uranium at higher concentration levels and in the presence of potentially mobilising organic ligands.

ACKNOWLEDGEMENTS

REFERENCES

Bennett, D.G., Read, D., Lawless, T.A. and Sims, R.J., 1992a. The migration of uranium through sandstone. U.K. Dep. Environ., London, Rep. No. DOE/HMIP/RR/92.101.

Bennett, D.G., Liew, S.K., Mawbey, C.S. and Read, D., 1992b. CHEMTARD — Theoretical overview. U.K. Dep. Environ., London, Rep. No. DOE HMIP RR 92.036, 53 pp.

Berry, J.A., Bond, K.A., Ferguson, D.R. and Pilkington, N.J., 1991. Experimental studies on the effects of organic materials on the sorption of uranium and plutonium. Radiochim. Acta, 52/53: 201–209.

Bidoglio, G., Offermann, P. and Saltelli, A., 1987. Neptunium migration in oxidizing clayey sand. Appl. Geochem., 2: 275–284.

Chandratillake, M.R., Falck, W.E. and Read, D., 1992. Guide to the CHEMVAL thermodynamic database. U.K. Dep. Environ, London, Rep. No. DOE/HMIP/RR/92.094, 24 pp.

Come, B. and Chapman, N.A. (Editors), 1991. Fourth natural analogue working group meeting and Poços de Caldas project final workshop. Comm. Eur. Commun.. Luxembourg, Rep. CEC No. EUR13014 EN, 284 pp.

Davis, J.A., James, R.O. and Leckie, J.O., 1978. Surface ionization and complexation at the oxide/water interface. II. Surface properties of amorphous iron oxyhydroxide and adsorption of metal ions. J. Colloid Interface Sci., 67: 90–107.

Djafer, M., Lamy, I. and Terce, M., 1989. Interaction of metallic cations with the hydrous goethite (α-FeOOH) surface. Progr. Colloid. Polym. Sci., 79: 150–154.

Economides, V., Dawes, A. and Read, D., 1990. Chemical modelling studies in support of HMIP probabilistic risk assessment. U.K. Dep. Environ., London, Rep. No. DOE/RW/90.001, 292 pp.

Grenthe, I., Lemire, R.J., Muller, A.B., Nguyen-Trung, C. and Wanner, H., 1992. Chemical thermodynamics of uranium. North-Holland Publishing Co., Amsterdam. 656 pp.

Hooker P.J., 1991. An overview and assessment of the British Geological Survey's research work on natural analogue studies in Great Britain. Radiochim. Acta. 52/53: 341–347.

Parkhurst, D.L., Thorstenson, D.C. and Plummer, L.N., 1980. PHREEQE — A computer program for geochemical calculations. U.S. Geol. Surv. PB81 167801, 195 pp.

Read, D. (Editor), 1991. CHEMVAL Project. Report on Stages 3 and 4: Testing of coupled chemical transport models. U.K. Dep. Environ., London, Rep. No. DOE/HMIP/RR/91.003, 240 pp.

Sandino, A., 1991. Processes affecting the mobility of uranium in natural waters. Ph.D. Thesis. Royal Institute of Technology, Stockholm (unpublished).

Thompson, B.G.J., 1987. The development of procedures for the risk assessment of underground disposal of radioactive wastes: Research funded by the Department of Environment 1982–1987. Rad. Waste Manage. Nucl. Fuel Cycle, 9: 215–256.

Williams, G.M., Higgo, J.J.W., Sen, M.A., Falck, W.E., Noy, D.J., Wealthall, G.P. and Warwick, P., 1991. The influence of organics in field migration experiments. Part 1. In situ tracer tests and preliminary modelling. Radiochim. Acta, 52/53: 457–463.

Wolery, T.J., 1988. EQ3/6 thermodynamic database — February 1988. Livermore Natl. Lab., Livermore, CA, Code Release 3245R54.